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A process for the liquefaction of lignocellulosic material

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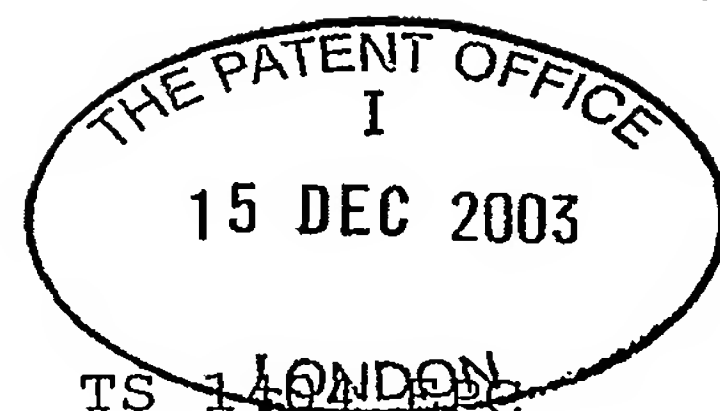
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A PROCESS FOR THE LIQUEFACTION OF LIGNOCELLULOSIC  
MATERIAL

Field of the invention

The present invention relates to a process for the  
liquefaction of lignocellulosic or cellulosic material.

Background of the invention

5 It is known to produce levulinic acid by controlled  
acid hydrolysis of lignocellulosic material. Levulinic  
acid is a useful compound, since its reactive nature  
makes it a suitable intermediate for the production of  
commercially interesting compounds. Reference is made to  
R.H. Leonard, "Levulinic Acid as Basic Chemical Raw  
Material", Ind. Eng. Chem., 48 (1956) 1331-1341, in this  
10 respect.

In US 5,608,105 for example, a process is described  
wherein levulinic acid is produced from cellulose or  
ligno-cellulose material by hydrolysing the material at  
a temperature between 210 and 230 °C in the presence  
15 of 1-5 % weight of mineral acid in a first reactor to  
obtain a hydroxymethylfurfural-containing intermediate  
product and further hydrolysing the intermediate product  
at a temperature between 195 and 215 °C in the presence  
of 3-7.5% weight of mineral acid in a second reactor. The  
20 temperature in the first and the second reaction vessel  
is controlled by injection of high pressure steam. The  
process pressure is therefore above 200 psig (14 bar g)  
in the second vessel and much higher in the first vessel.  
In US 6,054,611, a process is described wherein biomass  
25 containing cellulose and hemicellulose is mixed with

sulphuric acid to form an aqueous reaction solution having about 20-40% by weight of biomass and 10-30% by weight of acid. The reaction solution is first maintained below 60 °C to decrystallise the biomass and then heated to 80-200 °C to hydrolyse the biomass to form sugars, which then react to form levulinic acid.

In the above-described prior art processes, solid biomass or lignocellulosic material is used as starting material for the production of levulinic acid. Either high pressure or a high concentration of acid is needed to be able to convert the solid material. It would be advantageous to use liquefied lignocellulosic or cellulosic material as starting material for levulinic acid production processes or other chemical processes for the conversion of lignocellulose. A liquefied starting material for levulinic acid production or other biomass conversion processes will allow milder process conditions and allows the use of heterogeneous catalysis for further processing. It would further allow separation of contaminants from the desired components in the starting material.

Reference herein to liquefied (ligno)cellulosic materials is to (ligno)cellulosic material dissolved in a liquid medium. Liquefaction of solid (ligno)cellulosic material is typically achieved by mildly heating the (ligno)cellulose with an organic solvent in the presence of an acid catalyst. This treatment will result in some cleavage of covalent linkages of cellulose, hemicellulose and lignin and of covalent linkages between lignin and hemicellulose. Acids such as formic, acetic and propionic acid, ketones, aldehydes, sugars and lignin degradation products might be formed.

It is known that biomass or lignocellulosic material can be liquefied at ambient pressure and moderate temperature in the presence of an acid catalyst by using solvents.

5           In EP 472 474 A, for example, is described a process for liquefying lignocellulose substance by heating the substance at a temperature of 100 to 200 °C and ambient pressure in the presence of an acid catalyst and one or more polyhydric alcohols. Polyethylene glycol,  
10 polypropylene glycol, glycerin, ethylene glycol, 1,4-butanol, 1,6-hexanol and polycaprolactone are mentioned as possible polyhydric alcohols.  
In Bioresource Technology 70 (1999) 61-67, the use of  
15 cyclic carbonates such as ethylene carbonate and propylene carbonate as solvents for the liquefaction of lignocellulosic material in the presence of an acid catalyst at 120-150°C has been described.

Summary of the invention

20           It has now been found that it is possible to liquefy lignocellulosic or cellulosic material at mild conditions by using as solvent compounds that can be derived from biomass.

25           Accordingly, the present invention relates to a process for the liquefaction of lignocellulosic or cellulosic material, wherein solid lignocellulosic or cellulosic material is heated at a temperature in the range of from 100 to 300 °C in the presence of an acid catalyst and a solvent, wherein the solvent-to-solid material weight ratio is at most 50, the acid catalyst is  
30 present in a concentration of at most 50% by weight of acid based on the weight of solvent and acid, and the solvent is a compound obtainable by acid hydrolysis of lignocellulosic material or a compound that can be



derived from such compound by esterification, hydrogenation, dehydration, etherification, and/or dimerisation or oligomerisation.

5 An advantage of the process according to the present invention is that the solvent can be obtained from a subsequent biomass conversion process step. This means that the solvent is available (by simple recycle from the subsequent process step) and does not have to be removed from the liquefied biomass.

10 Detailed description of the invention

In the liquefaction process according to the invention, a compound obtainable by acid hydrolysis of lignocellulosic material or a compound that can be derived from such compound is used as solvent for  
15 (ligno)cellulose material.

The solvent may be a compound that can be directly obtained by acid hydrolysis of lignin, hemicellulose or cellulose or indirectly by subsequent esterification, hydrogenation, dehydration, etherification, and/or  
20 dimerisation or oligomerisation of a direct acid hydrolysis product. The solvent is preferably a compound that can be directly or indirectly obtained by acid hydrolysis of hemicellulose or cellulose. Examples of suitable solvents that can be obtained by acid hydrolysis  
25 of C5 sugars containing hemicellulose are furfural or its derivatives such as tetra hydrofurfuryl alcohol, furfuryl alcohol, diether of furfuryl alcohol, dimers or oligomers of furfural or furfuryl alcohol. Examples of suitable solvents that can be obtained by acid hydrolysis of  
30 cellulose or C6 sugars containing hemicellulose are 1,2,4-trihydroxybenzene or levulinic acid and its derivatives.

Preferred solvents are levulinic acid, esters of levulinic acid, compounds with 5 carbon atoms that can be derived from levulinic acid by hydrogenation and/or dehydration, or dimers or oligomers of hydrogenation products of levulinic acid. Examples of such preferred solvents are levulinic acid, alpha-angelicalactone and its oligomers, gamma-valerolactone, 1,4-pentanediol, 1-pentanol, alkyl levulinates, methyl tetrahydrofuran or a combination of two or more thereof. More preferred solvents are levulinic acid, ethyl levulinate, butyl levulinate, pentyl levulinate, gamma-valerolactone, 1,4-pentanediol, 1-pentanol, or a combination of two or more thereof. Gamma-valerolactone is a particularly preferred solvent.

Since the solvent has to be a liquid under the process conditions, oligomer solvents will typically contain at most ten monomers, preferably at most five.

The solvent and the solid (ligno)cellulosic material are mixed in a solvent-to-solid weight ratio of at most 50. Reference herein to the weight of the solid material is to the dry solid material. Since the amount of solvent should be sufficient to wet the solid material, the solvent-to-solid weight ratio will typically be above 3. Acid is added in such amount that the acid concentration is at most 50% by weight based on the weight of solvent and acid. Preferably, a strong mineral or organic acid is used. Reference herein to a strong acid is to an acid having a pKa value below 4.7. Examples of suitable strong acids are sulphuric acid, para toluene sulphonic acid, phenol sulphonic acid, phosphoric acid, hydrochloric acid, oxalic acid, formic acid, lactic acid and hydroxy acetic acid. Preferred strong acids are phosphoric acid, sulphuric acid, oxalic

acid, formic acid or a combination thereof. Particularly preferred is phosphoric acid. Compared to sulphur-containing acids, phosphoric acid has the advantage that recovered phosphoric acid can be converted into valuable products such as fertilizers. Another advantage of phosphoric acid is that it has a relatively high boiling point and thus remains liquid and stable at the process temperature at ambient pressure.

The acid concentration is preferably at most 20% by weight, more preferably in the range of from 0.5 to 10% by weight, even more preferably of from 1 to 5% by weight. The solvent-to-solid weight ratio is preferably in the range of from 3 to 20, more preferably of from 5 to 15. The mixture of solids, solvent and acid is thus a non-aqueous mixture that may contain a small amount of water that is brought in with the acid.

In order to facilitate liquefaction, the solid (ligno)cellulose material will typically be finely divided, for example in the form of powder (e.g. sawdust), wood chips, cutted stalks, fibres or paper or the like. It will be appreciated that a smaller size of the material will result in a reduced liquefaction time. A larger size of the material will probably have to be combined with some mechanical action during the liquefaction process in order to achieve liquefaction within an acceptable time.

The mixture of solids, solvent and acid is heated at a temperature in the range of from 100 to 300 °C, preferably of from 125 to 250 °C, more preferably of from 150 to 210 °C. It is an advantage of the process according to the invention that no high pressures are needed to achieve sufficient liquefaction of the solid material at an acceptable speed. The pressure is

preferably in the range of from 0.1 to 15 bar (absolute), more preferably of from 0.5 to 10 bar (absolute), even more preferably of from 0.8 to 3 bar (absolute). Ambient pressure is most preferred. With the liquefaction process according to the invention, a considerable amount of the solid is liquefied, typically at least 50% (w/w). It is possible to liquefy more than 80% (w/w) of the solid material at ambient pressure within a few hours.

The solvent used in the liquefaction process according to the invention may be obtained from a subsequent acid hydrolysis process, i.e from a process wherein the liquefied (ligno)cellulosic material is subjected to acid hydrolysis. One or more of the compounds obtained by the acid hydrolysis process are then recycled to the liquefaction reactor in a suitable amount. The solvent may also be a compound that can be derived from such acid hydrolysis compound by esterification, hydrogenation, dehydration, etherification, and/or dimerisation or oligomerisation. In that case, one or more of the compounds obtained by acid hydrolysis is/are converted prior to recycling to the liquefaction reactor.

The subsequent acid hydrolysis process is preferably a process for the preparation of levulinic acid from the liquefied lignocellulosic material. This may for example be a process as disclosed in US 5,608,105 or US 6,054,611.

Advantages of the use of solvents that are derived from a subsequent acid hydrolysis process is that the solvent does not need to be separated from the liquefied lignocellulosic material, since the compound does not negatively influence the subsequent process step. Another advantage is that the acid catalyst does not need to be

removed from the liquefied material, since the subsequent process is also a process using an acid catalyst.

#### Examples

5 The invention will be further illustrated by means of the following non-limiting example.

#### EXAMPLES 1-3

10 2 grams of dried birch (*Betula* spp.) sawdust and 20 grams of gamma-valerolactone ( $\gamma$ VL) and an amount of phosphoric acid (85% by weight) were loaded in a 30 ml glass flask. The flask was placed in a silicon oil bath and heated. The amount of phosphoric acid, temperature, and duration of the experiment were varied. The flasks were cooled with water to end the experiment. The percentage of residue was determined by vacuum-filtering the content of the flask, followed by washing the residue with 150 ml of acetone/water (9:1 v/v). The resulting residue was dried at 105 °C for 8 hours and weighed.

#### EXAMPLE 4

20 2 grams of dried birch (*Betula* spp.) sawdust, 10 grams of gamma-valerolactone, 10 grams of 1-pentanol and phosphoric acid were heated in an autoclave at a temperature of 230 °C during 16 minutes. The pressure reached 12.7 bar (absolute). The percentage of residue was determined as described above.

25 In Table 1 is shown the phosphoric acid concentration (based on the weight of solvent and acid), temperature, heating time and percentage of residue for each of the EXAMPLES 1 to 4.

Table 1 Liquefaction of biomass

EXAMPLE	pressure (bar a)	solvent	H <sub>3</sub> PO <sub>4</sub> conc. (%wt)	T ( °C)	time	residue (% wt)
1	1.0	γVL	3	200	1h	16
2	1.0	γVL	7	180	4h	10
3	1.0	γVL	3	184	3h	18
4	12.7	γVL/1- pentanol (50/50)	3	230	16 min	3







TS 1404 EPC

C L A I M S

1. A process for the liquefaction of lignocellulosic or cellulosic material, wherein solid lignocellulosic or cellulosic material is heated at a temperature in the range of from 100 to 300 °C in the presence of an acid catalyst and a solvent, wherein the solvent-to-solid material weight ratio is at most 50, the acid catalyst is present in a concentration of at most 50% by weight of acid based on the weight of solvent and acid, and the solvent is a compound obtainable by acid hydrolysis of lignocellulosic material or a compound that can be derived from such compound by esterification, hydrogenation, dehydration, etherification, and/or dimerisation or oligomerisation.
2. A process according to claim 1, wherein the solvent is furfural or a compound obtainable by hydrogenation, etherification and/or dimerisation or oligomerisation of furfural.
3. A process according to claim 1, wherein the solvent is levulinic acid, an ester of levulinic acid, a C5 compound obtainable by hydrogenation and/or dehydration of levulinic acid, or a dimer or oligomer of a C5 compound obtainable by hydrogenation of levulinic acid, preferably is levulinic acid, gamma-valerolactone, 1,4-pentanediol, 1-pentanol, ethyl levulinate, butyl levulinate, pentyl levulinate or a combination of two or more thereof, more preferably is gamma-valerolactone.
4. A process according to any one of the preceding claims, wherein the acid catalyst is a strong mineral or organic acid, preferably phosphoric acid, sulphuric acid,



oxalic acid, formic acid or a combination thereof, more preferably phosphoric acid.

5        5. A process according to any one of the preceding claims, wherein the acid catalyst is present in a concentration of at most 20% by weight, preferably of from 0.1 to 10% by weight, more preferably of from 0.5 to 5% by weight.

10       6. A process according to any one of the preceding claims, wherein the solvent-to-solid material weight ratio is in the range of from 3 to 20, preferably of from 5 to 15.

7. A process according to any one of the preceding claims, wherein the temperature is in the range of from 120 to 250 °C, preferably of from 150 to 210 °C.

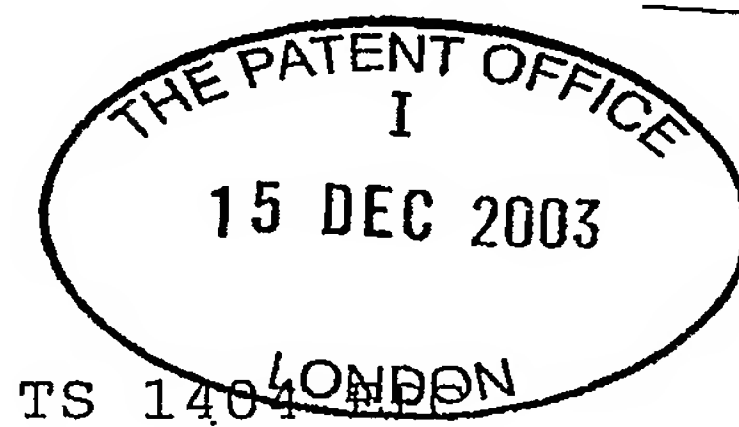
15       8. A process according to any one of the preceding claims, wherein the pressure is in the range of from 0.1 to 15 bar (absolute), preferably in the range of from 0.5 to 10 bar (absolute), more preferably in the range of from 0.8 to 3 bar (absolute), most preferably is  
20       ambient pressure.

9. A process according to any one of the preceding claims, wherein at least part of the liquefied lignocellulosic or cellulosic material is subjected to acid hydrolysis to form a product mixture comprising acid  
25       hydrolysis compounds, wherein at least one of the acid hydrolysis compounds, or a compound derived therefrom by esterification, hydrogenation, dehydration, etherification, and/or dimerisation or oligomerisation, is used as the solvent.

30       10. A process according to claim 8, wherein the product mixture comprises levulinic acid and wherein at least part of the levulinic acid, a compound derived therefrom

by esterification, hydrogenation, dehydration, and/or  
dimerisation or oligomerisation is used as the solvent





A B S T R A C T

A PROCESS FOR THE LIQUEFACTION OF LIGNOCELLULOSIC  
MATERIAL

A process for the liquefaction of lignocellulosic or cellulosic material, wherein solid lignocellulosic or cellulosic material is heated at a temperature in the range of from 100 to 300 °C in the presence of an acid catalyst and a solvent, wherein the solvent-to-solid material weight ratio is at most 50, the acid catalyst is present in a concentration of at most 50% by weight of acid based on the weight of solvent and acid, and the solvent is a compound obtainable by acid hydrolysis of lignocellulosic material or a compound that can be derived from such compound by esterification, hydrogenation, dehydration, etherification, and/or dimerisation or oligomerisation.

